

NANO BIOSENSORS: OPTICAL PROPERTIES OF CdTe/CdSe VERSUS CdSe/CdTe

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Abstract – Nanocrystals have recently attracted great interest in both fundamental research and technical applications in biomedicine. Type II quantum dots can be engineered to have effective band-gaps that are determined by the band offsets, which creates opportunities to tailor the properties of nanocrystals.

Keywords – Quantum dots, biosensors, luminescence

I. INTRODUCTION

Labeling and sensing methods that use fluorescence probes remain the cornerstone of most biological research protocols. In the 21st century, the progress in synthesis and optimization of semiconductor nanocrystals (or quantum dots, QDs) has opened the doors to an expanding variety of biological applications, like serving as specific markers for cellular structures and molecules, tracing cell lineage, monitoring physiological events in live cells, measuring cell motility, and tracking cells in vivo [1]. These nanometer-sized QDs are composed of periodic groups II–VI (e.g., CdSe) or III–V (e.g., InP) materials. They are robust fluorescence emitters with size-dependent emission wavelengths.

II. REVIEW OF LITERATURE

A. Advantages of Using QDs as Biosensors

Imaging techniques have traditionally used natural molecules that fluoresce, such as organic dyes and proteins that are found in jellyfish and fireflies. Each dye emits light over a wide range of wavelengths, so their spectra overlap. This makes it difficult to use more than three dyes at a time in order to tag and image different biological molecules simultaneously. The fluorescence of dyes also tends to fade away quickly over time. Organic dyes typically have narrow absorption spectra; they can only be excited within a narrow window of wavelengths. Moreover, they have asymmetric emission spectra broadened by a red tail, as depicted in Figure 1 [2].

Inorganic QDs can get around these problems; in addition to being brighter and living longer than their organic counterpart, QDs are highly stable against photobleaching, have a broader excitation spectrum and narrow, symmetric emission spectra. Effectively, nanocrystals can be excited by a single wavelength shorter than their emission wavelengths, with minimum signal overlap.

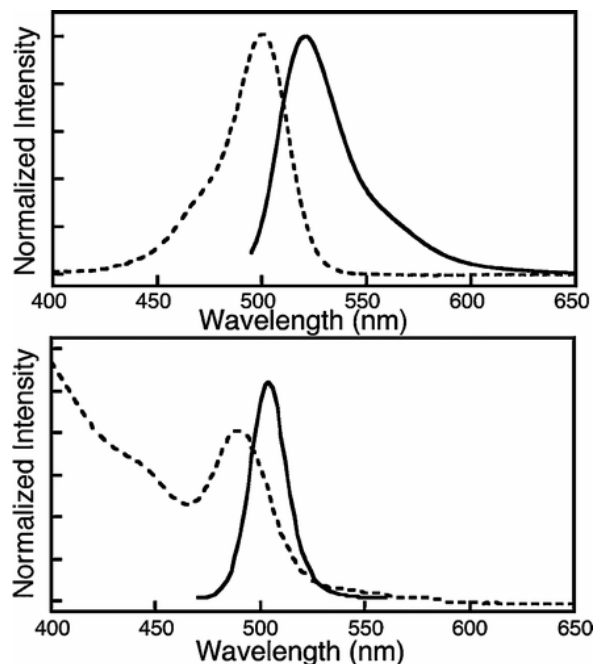


Figure 1. Excitation (dotted line) and fluorescence (solid line) spectra of fluorescein (top) and a typical water-soluble QD (bottom). The excitation wavelength was 476 nm and 355 nm for fluorescein and QD, respectively.

The fluorescence lifetime of QDs is 10 to 40 ns, which is significantly longer than typical organic dyes that decay on the order of a few nanoseconds. A mixture of QDs of different sizes can be excited by a light source with a single wavelength, allowing simultaneous detection and imaging of all different-color dots. When compared with commonly used fluorophores, such as rhodamine, fluorescein, and Alexa-Fluor, the photostability of QDs makes them attractive probes for imaging thick cells and tissue over long time periods—a challenging task that necessitates collection of multiple optical sections without damaging the specimen [3].

B. Disadvantages of Using QDs as Biosensors

QDs have some undesirable properties; one of these is called blinking — QDs randomly alternate between an emitting state and a non-emitting state — which imposes some limitations in QD applications requiring single-

molecule detection. Concerns have been raised about the toxicity of QDs, especially when they are used to study live cells and animals because they contain elements such as cadmium and selenium. However, when properly capped by both ZnS and hydrophilic shells, no acute and obvious CdSe QD toxicity has been detected in studies of cell proliferation and viability in live cells and animal models. To make QDs more useful for probing live cells and other biological applications, they need to be conjugated to biological molecules without disturbing the biological function of these molecules [1].

C. Other Applications of QDs

Quantum dots, particularly those that provide the hard-to-reach blue end of the spectrum, enable technological advances in the fields of full-color, flat-panel displays; ultrahigh-density optical memories and data storage; and backlighting; in addition to chemical and biological sensing and labeling. Research is currently underway to manufacture QD photovoltaics, lasers, and all-optical nano logic gates and switches.

D. How QDs Work

The properties of matter at nanometer-scales are governed by a complex combination of classical physics and quantum mechanics [4]. Quantum dots have a small, countable number of electrons confined in a small space. As in an atom, the energy levels in a QD become quantized due to the confinement of electrons. When the electron-hole pairs in the core of a QD are excited with a beam of light, they re-emit light (fluoresce) with a narrow and symmetric emission spectrum that depends directly on the size of the crystal. The smaller the dot the higher the energy and intensity of its emitted light. The color of the emitted light depends on the size of the QDs: the larger the dot, the redder the light. As the QDs shrink in size, the emitted light becomes shorter in wavelength, moving toward the blue. This means that QDs can be fine-tuned to emit light at a variety of wavelengths simply by altering the size of the core, and therefore constitute a set of multicolored molecular beacons for use in imaging [5].

Table 1. Relationship between size and photoluminescence for pure CdSe

size ^a (nm)	Size dispersity ^a (%)	λ_{abs} ^b (nm)	PL λ_{max} (nm)
3.0	3	505	520
5.0	4	615	630
6.0	5	634	648
8.8	10	661	672
10.5	7	672	683
13.4	9	681	698

Composition and size-tunable properties have become a hallmark of QDs and related nanostructures. An example is provided in Table 1, which describes the size and optical properties of CdSe (cadmium-selenide) [4].

E. Type-I and Type-II QDs

The QDs are classified into two types based on the properties of materials in the hetero-structured nanocrystal. In Type I QDs, the band offsets are such that the conduction band of the shell is of higher energy than that of the core and the valence band of the shell is of lower energy than that of the core. As a result, both electrons and holes are confined in the core. In Type-II QDs, both the valence and conduction bands in the core are lower (or higher) than the shell. As a result, one carrier is mostly confined to the core while the other carrier is confined to the shell. Type II QDs are expected to have many novel properties that are fundamentally different from the Type-I QDs because of the spatial separation of carriers [6].

III. PURPOSE OF THE STUDY

The purpose of the study was to examine type II QDs in the II-IV family; the study particularly focused on luminescence characteristics of cadmium telluride (CdTe) cadmium selenide (CdSe) core/shell variation. The goal is to develop the ability to tailor the properties and fabricate specific nanocrystals.

IV. METHODOLOGY

The method of molecular dynamics (MD) solves Newton's equations of motion for a molecular system, which results in trajectories for all particles considered in the system. Thus MD provides a tool suitable for simulating time-dependent processes at an atomic level, like the growth of crystals, the reordering of interfaces, the interaction between atoms and surfaces as well as the relaxation of core structures of lattice defects. QDs can be self-assembled through computer simulations in a variety of material systems and geometries.

A series of MD simulations was performed in order to examine QDs are self-assembled using the Stranski-Krastanov growth mode, and their density and uniformity was repeatedly and accurately tuned by controlling specific growth parameters. The Stillinger-Weber interatomic potential has been used to perform medium scale computer simulation of the island structure. 3-D visualization depicts the 3-D confined wave functions. Optical transitions are computed and sorted into dark and light lines. Absorption curves are computed for different polarizations and orientations.

The study involved 4.5-nm CdTe and CdSe cores coated with 0.6-nm CdSe and CdTe shells, respectively. At these core sizes and shell thicknesses, the core-shell dots of both

types have the same overall diameter of 5.1 nm and the same elemental composition of 58% Se and 42% Te. This is in agreement with calculations based on either crystal lattice parameters or bulk CdSe and CdTe densities that yield composition results which are within 5% of each other.

V. RESULTS AND DISCUSSION

Emission spectra were taken using an excitation wavelength of 475 nm with excitation and emission slit widths set at 2.0 nm. Recorded spectra were corrected for the wavelength dependence of detector response. The electron energy spectra in CdTe/CdSe versus CdSe/CdTe semiconductor QDs is depicted. The optical characteristics are evaluated by the photoluminescence method. Figure 1 shows the x-ray power diffraction data for pure CdSe and pure CdTe, and Table 2 provides a summary of optical properties of pure CdTe and pure CdSe.

Figure 2 shows the schematic structure of the two different types of nanocrystals and their fluorescence emission spectra. The CdTe/CdSe core/shell nanocrystals are fluorescent with an emission peak at 700 nm, but the reversed core/shell CdSe/CdTe nanocrystals show no band-edge luminescence.

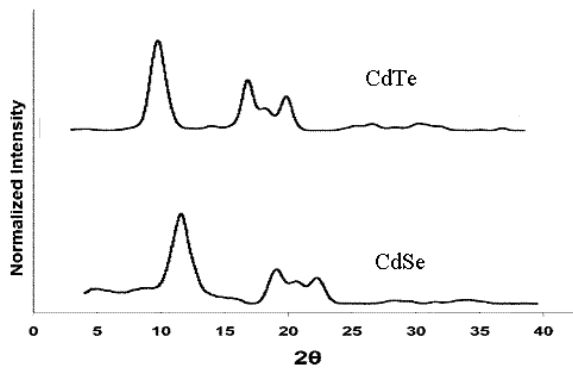


Figure 1. X-ray power diffraction data for pure CdSe and pure CdTe.

Table 2. Summary of optical properties of pure CdTe and CdSe

Material	Index of Refraction	β (Two-photon absorption coefficient, cm/MW)
CdTe	2.318	0.19
CdSe	2.739	0.12

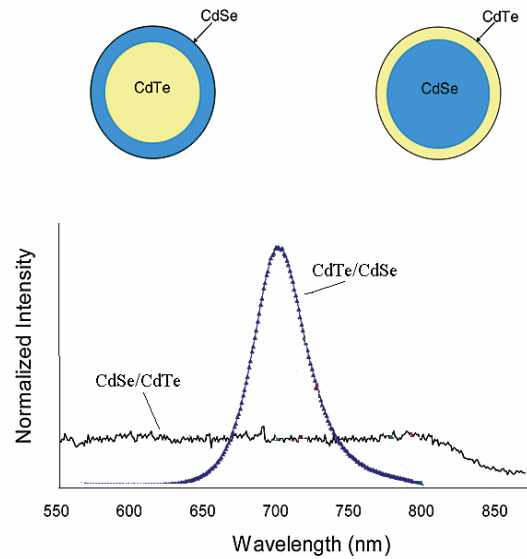


Figure 2. Emission spectra for CdSe and CdTe core/shell nanocrystals.

This is in agreement with theory; CdTe has a lower band-gap than CdSe and is unable to provide an effective shell. The core of the QD when contained within a protective inorganic shell with a higher electronic band gap than the core, it improves the confinement of the electron-hole pairs and therefore increases the intensity of the fluorescence [7].

VI. SUMMARY

Colloidal QDs possess numerous physical and optical properties that are ideal for multiplexing signal channels for parallel detection and labeling applications in biomedicine. Because QDs are extremely bright and photostable, they can be used as cell markers for long-term studies such as cell-cell interactions, cell differentiation and cell lineage tracking. Emission in Type II hetero-structured QDs, originates from the radiative recombination of the electron-hole pair across the core/shell interface [8]. The energy of emission depends on the band offsets of the two materials making up the core and the shell. Type II QDs can thus emit at energies that are lower or higher than the band-gap of either material. This is demonstrated in Figure 2, where CdTe/CdSe QDs emit at a wavelength longer than either CdTe or CdSe. Type II QDs can be engineered to have effective band-gaps that are determined by the band offsets. This creates opportunities to further research more combinations to tailor the properties of nanocrystals. Tuning the chemistry to optimize imaging and detection conditions will be the key to use of QDs in biomedicine.

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